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Climatic and sea-level control of Jurassic (Pliensbachian) clay mineral sedimentation in the Cardigan Bay Basin, Llanbedr (Mochras Farm) borehole Wales

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ABSTRACT

Early Jurassic climate is characterized by alternating cold and warm periods highlighted by studies based notably on oxygen isotopes measured on belemnite guards and other marine invertebrate shells. These climatic changes include changes in the hydrological cycle, and consequently weathering and runoff conditions. In order to clarify the erosion and weathering conditions during the Pliensbachian, this study determined the mineralogical composition of the clay fraction of 132 samples taken from the entire stage drilled in the Llanbedr (Mochras Farm) borehole (Cardigan Bay Basin). The clay mineral assemblages are composed of

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various proportions of chlorite, illite, illite/smectite mixed-layers (R1 I–S), smectite and kaolinite, with possibly occasional traces of berthierine. The occurrence of abundant smectite indicates that the maximum burial temperature never exceeded 70°C. Consequently, clay minerals are considered mainly detrital, and their fluctuations likely reflect environmental changes. The variations in the proportions of smectite and kaolinite are opposite to each other. Kaolinite is particularly abundant at the base of the *jamesoni* Zone, in part coinciding with the $\delta^{13}C$ negative excursion corresponding to the Sinemurian/Pliensbachian Boundary Event, and through the *davoei* Zone, whilst smectite is abundant in the upper part of *jamesoni* and base of *ibex* zones and through the *subnodosus*/*gibbosus* subzones of the *margaritatus* Zone. The kaolinite-rich intervals reflect an intensification of hydrolysis and an acceleration of the hydrological cycle, while the smectite-rich intervals indicate a more arid climate. The *spinatum* Zone is characterized by a distinct clay assemblage with abundant primary minerals, R1 I–S, kaolinite reworked from previously deposited sediments or from Palaeozoic rocks, and probably berthierine originating from contemporaneous ironstone-generating environments of shallower waters. This mineralogical change by the end of the Pliensbachian likely reflects a transition from a dominant chemical weathering to a deeper physical erosion of the continent, probably related to a significant sea-level fall consistent with a glacio-eustatic origin.

Keywords: Clay minerals, clay sedimentation, Pliensbachian, Early Jurassic, palaeoclimate

INTRODUCTION

The Early Jurassic is characterized by significant environmental changes, the most prominent of these being the Toarcian Oceanic Anoxic Event (T-OAE). This early Toarcian global event has been the subject of numerous studies in various sedimentary basins, which have

highlighted the important role of global warming, attested by a dramatic increase in the temperature of ocean waters and enhanced hydrolysis on continents (e.g. Jenkyns 1988, 2010; Raucsik & Varga 2008; Dera et al., 2009; Harazim et al., 2013; Hermoso & Pellenard, 2014; Korte *et al.*, 2015; Them *et al*. 2017; Müller *et al*., 2017; Izumi *et al.* 2018). By contrast, Pliensbachian deposits have been less studied, while this stratigraphic interval also shows significant climatic fluctuations (Gómez *et al*., 2016a; Korte *et al*., 2015; Price *et al.*, 2016). Most studies relating to climate change during the Pliensbachian period have been carried out using temperature proxies, notably $\delta^{18}O$ measured on several calcite hard parts of molluscs and brachiopods. Highlighted are several cold intervals, the most prominent of these occurring in the latest Pliensbachian, time equivalent to the *spinatum* Zone (Bailey *et al*., 2003; Rosales *et al*., 2004; Dera et al., 2009; Suan *et al*., 2010; Harazim *et al.*, 2013; Gómez *et al*., 2016a; Bougeault *et al*., 2017; Arabas *et al*., 2017). This cold episode could have been responsible for the formation of ice at high palaeolatitudes (Suan *et al*., 2010), consistent with the supposed record of prominent obliquity cycles expressed as detrital input at mid-latitudes by the end of the Pliensbachian (Boulila & Hinnov, 2017). By contrast, the stratigraphic interval including the *davoei* Zone corresponds to a warmer period characterized by an acceleration of the hydrological cycle (Rosales *et al*., 2004; Dera *et al*., 2011; Silva & Duarte, 2015; Price *et al*., 2016; Bougeault *et al*., 2017). However, fluctuations of humidity/aridity are still little explored or discussed. The current study attempts, through the identification of detrital clay mineral assemblages of Pliensbachian sediments from the Llanbedr (Mochras Farm) borehole, hereafter referred to as 'Mochras', to estimate the intensity of physical and chemical weathering as well as the intensity of hydrolysis and runoff.

GEOLOGICAL BACKGROUND

The Mochras borehole drilled in 1968/1970 on the west coast of Wales (Fig. 1) yielded a *ca* 1.3 km thick, biostratigraphically complete succession of calcareous mudstone and clay-rich limestone, deposited in the Cardigan Bay Basin and representing almost the entire Early Jurassic (Woodland, 1971; Dobson & Whittington, 1987; Hesselbo *et al*., 2013; Copestake & Johnson, 2014). The Cardigan Bay Basin was located close to the emergent Welsh Massif at a palaeolatitude estimated between 35° and 40°N (Fig. 2).

The Early Jurassic succession at Mochras is remarkable for its relatively uniform argillaceous lithology, for its thickness, approximately three times those of coeval sediments from European boreholes or coastal outcrops (Hesselbo et al., 2013), and for the absence of any evidence of significant hiatus or scouring (Ruhl et al., 2016). This study focused on the 400 m thick Pliensbachian interval predominantly characterized by more or less pronounced lithological couplets of pale grey limestone and dark brown to grey, locally faintly laminated, mudstone, with individual lithological couplets commonly showing gradual transitions between these end-members (Ruhl et al., 2016). The thickness of the lithological couplets varies between 90 cm at the base of the Pliensbachian to 30 cm in its upper part. Typically, the $CaCO_3$ content ranges between 10% and 65%. Organic matter content is generally low, except in some laminated dark mudstones containing up to 2.1% total organic carbon (TOC). Thin-section observations reveal early diagenetic feature such as calcite cementation and the common occurrence of framboids of pyrite resulting from the reduction of sulphate (Ruhl et al. 2016).

METHODS

The entire Pliensbachian succession was sampled at an average step of 3 m. A total of 132 samples were then analyzed using x-ray diffraction (XRD). After a gentle, manual crush in a mortar, powdered samples were decarbonated with a 0.2M HCl solution. The fraction below two microns (clay sized particles), was extracted with a syringe after decantation of the suspension for 95 minutes following Stokes law, and then centrifuged. Clay residue was then smeared on oriented glass slides and run in a Bruker D4 Endeavour diffractometer (Bruker, Billerica, MA, USA) with CuK_{α} radiations, LynxEye detector and Ni filter under 40 kV voltage and 25 mA intensity (Biogeosciences Laboratory, Université Bourgogne Franche-Comté). Samples were scanning from a range of 2.5° to 28° for each analysis. Three runs were performed for each sample to discriminate clay phases: (i) air-drying; (ii) ethylene-glycol solvation; and (iii) heating at 490°C, as recommended by Moore & Reynolds (1997). Clay minerals were identified using their main diffraction (d_{001}) peak and by comparing the three diffractograms obtained. Estimated proportions of each clay mineral were performed using the MacDiff 4.2.5 software (Petschick, 2000) on glycolated diffractograms. As the main (d_{001}) peak of kaolinite and the (d_{002}) peak of chlorite are overlapping, a deconvolution procedure was applied on the (d_{004}) peak area of chlorite (3.54 Å) and (d_{002}) peak area of kaolinite (3.57 Å) to estimate properly both mineral's proportions using the 7.1 peak ($d_{001kaolinite} + d_{002chlorite}$). Chlorite percentage was calculated using the mean between (d_{001}) and (d_{002}) chlorite peak areas considering that the chemical nature in the chlorite impacts the (d_{001})/(d_{002}) ratio (Moore & Reynolds, 1997). The K/I and Sm/K ratios based on (d_{001}) peak area of each mineral was systematically calculated. Beside clay mineral analyses, $CaCO_3$ content of most samples was measured using a Bernard calcimeter device.

Observations by transmission electron microscopy (TEM) were performed using a Hitachi H7500 transmission electron microscope (Hitachi, Tokyo, Japan) on a DimaCell Platform installed at the 'Institut National de la Recherche Agronomique' (INRA; Dijon, France) to examine the morphology of clay particles from six representative samples.

RESULTS

The main clay minerals identified are: (i) R0 type illite-smectite mixed-layer (17 Å based on the glycolated run condition) referred to smectite for the following sections; (ii) R1 type illite-smectite mixed-layer (around 11.5 Å on air-drying conditions and 13 Å after ethylene-glycol solvation); (iii) chlorite (14.2 Å, 7.1 Å, 4.7 Å and 3.54 Å peaks); (iv) illite (10 Å, 5 Å, 3.33 Å peaks) and (v) kaolinite (7.18 Å and 3.58 Å peaks). Clay mineral assemblages of Pliensbachian sediments from the Mochras borehole mainly comprise chlorite (traces to 15%), illite (20 to 70%), R1 type illite-smectite mixed-layer (R1I-S; 0 to 27%), R0 type illite-smectite mixed-layer, hereafter called smectite (0 to 75%) and kaolinite (0 to 32%; Fig. 3). Small proportions of quartz and feldspar are systematically present in the clay fraction. A zeolite from the clinoptilolite-heulandite group characterised by the (020) reflection at 8.99 Å (Fig. 3) occurs particularly in the top *margaritatus* Zone and the *spinatum* Zone, and occasionally from top *ibex* to base *margaritatus* zones (Fig. 3). It is also suspected that the occurrence of small quantities of a 7 Å Fe-Mg mineral that may correspond either to odinite, berthierine or to a 7 Å/14Å interstratification (Beaufort et al., 2015). This mineral is not easy to identify in the presence of chlorite and kaolinite, because the main diffraction peak (001) at 7.05 Å is very close to the main diffraction peak of kaolinite and the (002) reflection of chlorite (Hornibrook & Longstaffe, 1996). However, after heating, a reflection at 6.99Å is observed that suggests the presence of berthierine, as the (001) peak at 7.05 Å of this mineral tends to shift slightly towards smaller d-values (Taylor, 1990). Consequently, on the heated

x-ray diagram it was observed that a band comprising a succession of three peaks which likely reflect the co-existence of chlorite, the remaining kaolinite and likely berthierine although a more precise identification of this mineral is needed (Fig. 3). Given the superimposition of the diffraction peaks, we could not quantify separately berthierine from kaolinite and chlorite, but its proportions probably never exceed 5 to 10%. The occurrence of this mineral is restricted to the base of the *jamesoni* Zone (*taylori*/*polymorphus* subzones) and the upper part of the *spinatum* Zone (Fig. 4).

Huge fluctuations in the relative proportions of clay minerals are recorded throughout the core (Fig. 4). The main features are the coeval variations between kaolinite, chlorite and the 7 Å Fe-Mg mineral, while smectite and kaolinite are inversely related. The proportions of illite are relatively stable from the base of the Pliensbachian to the middle part of the *margaritatus* Zone, but at the top of this zone, the proportion of illite decreases sharply in favour of smectite, above which the proportion of this mineral increases again in the *spinatum* Zone. R1 type illite/smectite mixed-layers (I-S) are fairly abundant in three intervals: (i) base of the *jamesoni*; (ii) top of *ibex/davoei* Zone; and (iii) top of *spinatum* Zone. In the first two intervals, the I-S abundance increase is in parallel with kaolinite, while in the *spinatum* Zone, where the proportions of I-S are particularly high, the increase occurs in parallel with illite and chlorite (Fig. 4).

The evolution of the proportions of chlorite and kaolinite shows two large cycles with a minimum around the *jamesoni/ibex* transition, and another within the *margaritatus* Zone, separated by a maximum abundance of these minerals centered on the *davoei* Zone. These minerals are relatively abundant in the lowermost Pliensbachian and in the *spinatum* Zone

(uppermost Pliensbachian). Since smectite shows a reverse correlation with kaolinite, the evolution of the proportions of this mineral is also in the form of two large cycles (Fig. 4).

The carbonate content of the studied sediments varies between 10% and 87% (Fig. 5). There is an obvious relationship between the $CaCO_3$ content of sediments and the clay mineral assemblages. The kaolinite-rich interval centered on the *davoei* Zone is markedly depleted in carbonate. As a result, the two large cycles marked by low proportions of chlorite and kaolinite are enriched in smectite and carbonate as also observed by Ruhl et al., (2016) using Ca content from x-ray fluorescence spectrometry.

The observation of clay minerals using TEM reveals that most particles show anhedral shape except some particles of kaolinite which are often sub-hexagonal (Fig. 6). Crystalline growth around the particles or perfectly euhedral particles was not observed. These observations also made it possible to affirm that the particles clearly fit into the less than 2 μm fraction.

DISCUSSION

Influence of burial diagenesis

Occurrence of smectite

Before examining the significance of clay minerals in terms of palaeoclimate and palaeoenvironment, it is important to ensure that they are dominantly detrital in origin without any significant influence of burial diagenesis. Smectites are known to be particularly sensitive to burial diagenesis and transform into R1 I-S by illitization processes with temperatures over 60 to 70°C (Merriman & Frey, 1999; Lanson *et al.*, 2009; Środoń *et al*., 2009; Dellisanti *et al*., 2010). As a result, the abundance of smectite from the lowermost

Pliensbachian (base of the *jamesoni* Zone) and throughout the core suggests that the maximum burial temperatures of the Pliensbachian sediments never exceeded 60 to 70°C. The occurrence of smectite is consistent with low values of T_{max} measured on the organic matter of the Pliensbachian mudrocks or immediately above in organic matter-rich sediments of the T-OAE. In the Pliensbachian, T_{max} values range between 421°C and 434°C indicating that organic matter is immature (Van de Schootbrugge *et al*., 2005). Similarly, in the T-OAE organic matter-rich shales, T_{max} values lie between 413 and 441°C (Xu *et al*., 2018). These data confirm a weak influence of thermal diagenesis linked to burial. Vitrinite reflectance (R_0 max) data suggest a maximal burial temperature of the Pliensbachian sediments of around 65°C (Holford *et al*., 2005). This temperature is compatible with the observed clay mineral assemblages, notably the occurrence of smectite (Dellisanti *et al*., 2010), although Holford *et al*., (2005) suspected the vitrinite reflectance values to be too low and questioned their reliability. According to new organic matter and clay mineral data, the temperatures deduced from vitrinite reflectance by these authors do seem to be realistic.

The co-variation between chlorite and kaolinite/berthierine

The suspected presence of berthierine is also an argument in favour of a low thermal influence, since this mineral transforms into chamosite (iron-rich chlorite) when the temperature approaches 100 °C (Velde, 1989; Storey, 1990 *in* Jeans 2006; Hornibrook & Longstaffe 1996; Beaufort et al., 2015). Although it cannot be excluded that some of the chlorite is derived from the transformation of berthierine into chamosite (Beaufort et al., 2015), remaining berthierine at depth indicates low maximum burial temperatures. The simultaneous presence of chlorite, kaolinite, berthierine and perhaps chamosite; minerals whose diffraction peaks are superimposed, raises the question of the significance of the co-

variation of chlorite and kaolinite. In a context where clay assemblages are dominated by detrital inputs, it is difficult to explain this co-variation, as is discussed fully below.

In summary, clay mineral assemblages do not appear to be altered by a significant influence from burial diagenesis. Consequently their fluctuations can be interpreted in terms of environmental changes that occurred during the Pliensbachian.

Authigenic minerals

Clinoptilolite-heulandite

Authigenic growth of clay minerals during early or late diagenesis may change significantly the primary mineralogical composition of clay assemblages. Authigenic zeolite of the clinoptilolite-heulandite group is common in Cenozoic oceanic (hemi)pelagic sediments (e.g. Bohrmann *et al*., 1989; Gingele & Schulz, 1993; Nähr *et al*., 1998). This mineral is also common in Late Cretaceous chalk of NW Europe (Pomerol & Aubry, 1977, Louail, 1979; Deconinck & Chamley, 1995), and in some formations of the Upper Jurassic to Lower Cretaceous in southern England (Brown *et al*., 1969), but this mineral has never been identified in Lower Jurassic sediments of north-western Europe. The authigenic formation of clinoptilolite at relatively low temperature is demonstrated in most sediments (Nähr *et al*., 1998). In particular, the occurrence of euhedral crystals which sometimes grow within foraminifera tests constitutes the most convincing argument for authigenesis (Louail, 1979; Karpoff *et al*., 2007). The origin of the silica necessary for the growth of these minerals is potentially twofold: it can come from the alteration of volcanic glasses; or from siliceous organisms including sponges, diatoms and radiolarians. Particles of volcanic origin have never been described in Pliensbachian sediments drilled at Mochras. At the scale of western

Europe, there are no tangible elements to identify explosive volcanic activity at this time. Therefore, it is likely that the silica is of biogenic origin. In that case, clinoptilolite can be taken as a proxy of enhanced productivity of siliceous organisms (Karpoff *et al*., 2007). Whatever its origin, clinoptilolite/heulandite formation seems to be favoured in slowly deposited sediments (e.g. Diekmann *et al*., 2004). Knowing the thickness of sediments corresponding to each ammonite zone and the duration of each zone inferred from cyclostratigraphic analyses (Ruhl *et al*., 2016), it is possible to estimate a mean sedimentation rate for each ammonite zone by assuming an equal compaction for the whole of the Pliensbachian. The mean sedimentation rate (after compaction) in the *jamesoni*, *ibex* and *margaritatus* zones is of the same order of magnitude, 46.7 m/Myr, 50.5 m/Myr and 45.4 m/Myr respectively. The sedimentation rate is slightly higher in the *davoei* Zone (57.5 m/Myr) but inferred to be significantly lower in the *spinatum* Zone (26.4 m/My) where clinoptilolite is mainly present suggesting that, as is the case in more recent sediments, the authigenesis of this mineral was favoured by slow deposition.

Berthierine

Berthierine is an iron-rich 1:1 type layer silicate commonly occurring in ooidal ironstones deposited in shallow, high energy marine environments (Bhattacharyya, 1983; Taylor & Curtis, 1995; Hornibrook & Longstaffe, 1996; Donaldson *et al*., 1999; Kozłowska & Maliszewska, 2015). Berthierine should be stable under anoxic conditions and its precipitation is thought to take place from reducing pore fluids in the absence of bacterially mediated sulphate reduction. During suboxic diagenesis, berthierine formed at the expense of iron oxide and detrital clay including kaolinite (Bhattacharyya, 1983; Rivard *et al*., 2013). The relatively deep, low energy depositional environment of the Cardigan Bay Basin at Mochras is not typical for the formation of berthierine, but this mineral is common in Lower

Jurassic ooidal ironstone outcropping in the British Isles (e.g., East Midlands Platform, Somerset) and deposited in shallower environments (Taylor & Curtis, 1995; Jenkyns & Clayton, 1997; Jeans, 2006).

There are no ironstones described in the Pliensbachian of the Mochras borehole, but laterally, in shallower depositional environments such those of the Cleveland Basin and other areas of Central and Southern England, this lithofacies is notably common in the *spinatum* Zone (Whitehead *et al*., 1952; Howard, 1985; Jenkyns & Clayton, 1997; Powell, 2010; Korte & Hesselbo, 2011), precisely in the stratigraphic interval where berthierine likely occurs in the Mochras borehole. Therefore, it is probable that the small quantities of berthierine occurring in Pliensbachian sediments at Mochras have been reworked and transported from the shallower areas of the basin margins especially as a result of low relative sea-level. According to Th/K ratios measured by gamma-ray spectrometry in Lower Jurassic of the Cleveland Basin, there is strong evidence that the ironstone originally contained significant concentrations of detrital kaolinitic/bauxitic material (Myers, 1989). It is therefore likely that kaolinite also originated at least in part from shallow environments, notably during regressive periods.

Environmental significance of clay mineral assemblages

Detrital sources and origin of clay minerals

Although clay minerals may be long transported and deposited away from their sources, given the palaeogeographic context (Fig. 2), the nearby Welsh Massif appears to be the most likely terrigenous source of sediments deposited in the Cardigan Bay Basin. Other detrital sources including in particular the Irish Massif could also have contributed to the clay

sedimentation, but for the time being, there is no evidence to distinguish the detrital sources. Chlorite and illite (primary minerals) are generally derived from the physical erosion of the bedrock consisting of magmatic, metamorphic and high-grade diagenetic sedimentary rock (Chamley, 1989). On the Welsh Massif, Lower Paleozoic mudrock mainly contains mica-illite and chlorite reflecting deep burial and low-grade metamorphism (Merriman, 2006). This is the case on most Variscan massifs in Europe and as a result, reflecting the physical erosion of Palaeozoic and older rocks in most Mesozoic sedimentary succession of north-western Europe, the proportions of chlorite and illite generally fluctuate in parallel. This is the case here except in the *ibex* and *davoei* zones where the proportions of chlorite increase while those of illite do not change significantly.

In sediments, smectites have various origins. This mineral group is most often reworked from soils where the clay formed under warm and seasonally humid climate (detrital origin), but smectite can also be formed in marine environments either at the expense of volcanic glass or as an authigenic phase in slowly deposited sediment (Deconinck & Chamley, 1995). The Pliensbachian sediments studied here do not show any evidence of volcanic origin and were rapidly deposited with high sedimentation rates responsible for the particularly great thickness (400 m) of the Pliensbachian. Sediments from the *spinatum* Zone were apparently deposited more slowly, considering the duration of this zone estimated to 1.4 Myr (Ruhl *et al.*, 2016), and its relatively reduced thickness. However, the proportion of smectite, not exceeding 20%, is low in this stratigraphic interval, suggesting the absence of clay mineral authigenesis. No obvious correlation is observed between zeolite and smectite in the core. The TEM observations reveal that smectite (I-S R0) shows a fleecy shape (Fig. 6) without any crystalline overgrowth thus suggesting a detrital origin (Chamley, 1989). Consequently, it is argued that most smectitic minerals detected here originated from

pedogenic blankets developed over the Welsh or Irish massifs during periods of warm and seasonally humid climate.

In sediment, kaolinite commonly has a dual origin. Firstly, as is the case for illite or chlorite, it can be reworked from kaolinite-bearing sedimentary rocks outcropping on the continents. For example, kaolinite may be reworked from sandstones where its authigenic formation is common as pore filling booklets, such as Devonian (Old Red Sandstone) and Carboniferous sandstones from southern England and Wales (Hillier *et al*., 2006; Shaw, 2006; Spears, 2006). Secondly, kaolinite may also originate from soils formed in a hot and regularly humid climate (Chamley, 1989; Ruffell *et al*., 2002). In both cases, increasing proportions of kaolinite in a sedimentary succession suggest enhanced runoff and erosion and/or hydrolyzing climate. Finally, R1 I-S mixed-layers are interpreted as the result of the moderate weathering of illite.

Climatic influences

The opposite evolution of smectite and kaolinite proportions suggests the alternation of wet periods rich in kaolinite, and drier periods rich in smectite. These apparent climatic fluctuations are discussed below in the light of data from other sedimentary basins or obtained through other climate proxies.

Kaolinite-rich intervals

There are two kaolinite-rich intervals as shown by the K/I and Sm/K ratios (Fig. 5). The most prominent of these straddles the uppermost part of the *ibex* Zone and the *davoei* Zone. This result was expected since this stratigraphic interval is known to be enriched in kaolinite in sections located at palaeolatitudes between 30 and 40°N (Dera *et al*., 2009). These authors

also showed, by comparison with other proxies including $^{87}Sr/^{86}Sr$, Mg/Ca and stable isotopes, that kaolinite is a reliable indicator of the climate that prevailed during the Pliensbachian/Toarcian interval. More recently, the detailed study of the clay mineralogy of two boreholes drilled in the Paris Basin clearly show a sharp increase of kaolinite in the *davoei* Zone (Bougeault *et al*., 2017). As a result, the new mineralogical data obtained from the Mochras borehole are consistent with previously published data and confirm warmer and wetter climate of the stratigraphic interval corresponding to the *davoei* Zone (Price *et al*., 2016). A more humid climate is probably responsible for enhanced runoff and high detrital input of clay minerals. Through the *ibex* zone, the gradual increase in the proportions of kaolinite probably reflect its progressive formation in soils under a more and more regularly humid climate. As a consequence, higher runoff is likely partially responsible for the dilution of the carbonate sedimentation and the relatively low carbonate content that characterized the stratigraphic interval including the *davoei* Zone (Fig. 5). This result is also consistent with the significant depletion of Ca measured by XRF from the *davoei* Zone (Ruhl *et al*., 2016). In this interval, higher runoff may be also responsible for the observed increasing sedimentation rate. However, the enrichment in chlorite in this stratigraphic interval is surprising because chlorite is an unstable mineral in a very hydrolyzing climate. This suggests that some of the chlorite does not have a detrital origin but could result from the transformation of berthierine into chamosite.

The other kaolinite–rich interval occurs at the base of the *jamesoni* Zone, where clay assemblages are similar to those encountered in the *davoei* Zone. Compared with the *davoei* Zone, this interval likely corresponded also to a wetter or even warmer climate. The increase in kaolinite at the base of the *jamesoni* Zone is less documented, but a slight increase of the K/I ratio was also identified in the Sancerre borehole located south of the Paris Basin

(Bougeault *et al.*, 2017). According to the cyclostratigraphic analyses performed by Ruhl et al., (2016), the duration of this kaolinite-rich package of sediments lasted about 400 ky. Interestingly, kaolinite enrichment occurred during the SPBE (Sinemurian/Pliensbachian Boundary Event) which coincides with a $\delta^{13}C$ negative excursion of 2 to 4‰ in marine calcite and organic matter (Jenkyns et al., 2002; van de Schootbrugge *et al*., 2005; Woodfine *et al*., 2008; Korte & Hesselbo, 2011; Armendariz *et al*., 2012; Franceschi *et al*., 2014; Korte *et al*., 2015; Price *et al*., 2016; Peti *et al*., 2017). This shift is also seen in the $\delta^{13}C$ of wood, reflecting global atmospheric change and a rearrangement of the global exogenic carbon cycle, possibly by the release of isotopically depleted carbon into the ocean–atmosphere system (Korte & Hesselbo, 2011; Ruhl *et al*., 2016). The important change in the mineralogical composition of the clay assemblages confirms that the weathering conditions in continental areas, which are themselves dependent on climate, have changed at least during part of the SPBE.

Smectite-rich intervals

The abundance of smectite was unexpected in that it is usually illite and kaolinite that dominate Lower Jurassic clay assemblages (e.g. Deconinck & Bernoulli., 1991; Debrabant *et al*., 1992; Deconinck *et al*., 2003, Jeans, 2006; Raucsik & Varga, 2008; Dera *et al*, 2009; Fantasia et al., 2018a,b). In the Jurassic of the Paris Basin, smectite only becomes occasionally abundant in sections or boreholes located close to the London–Brabant Massif, which was the main source of this mineral group (Pellenard & Deconinck, 2006; Hesselbo *et al*., 2009). In the Pliensbachian of the Paris Basin, smectite is restricted to the northern part, and only present during inferred periods of low sea-level when the London Brabant massif was emerged. By contrast, during highstand of sea-level, illite and kaolinite prevailed hypothetically because of the flooding of the smectite-rich lowlands covering this massif

(Bougeault *et al*., 2017). In the Pliensbachian of the Cardigan Bay Basin, there are two main smectite rich intervals, the most prominent of these occurs during the *subnodosus-gibbosus* subzones of the *margaritatus* Zone, while the second straddles *jamesoni* and *ibex* zones (Figs 4 and 5). A third thin smectite-rich interval occurs just above the Sinemurian/Pliensbachian transition.

Given the paleogeographic context, the very high sedimentation rate and the absence of identified volcanic influences, it is likely that the smectites are essentially detrital. The old metamorphosed rocks and the magmatic rocks that formed the emergent Variscan massifs cannot contain significant quantities of this mineral. Consequently, it is likely that smectite results from the erosion of soils formed under warm and seasonally humid (possibly monsoon-like) climates (Raucsik & Varga, 2008). Such seasonality is supported by documentation of well-expressed tree rings from fossil wood in the Cleveland Basin (Morgans *et al*., 1999), although samples studied thus far from the Early Jurassic are restricted to the lower *margaritatus* interval Thus, the smectite intervals seem to correspond to semi-arid periods. The top of the *margaritatus* Zone (*subnodosus/gibbosus* subzone) corresponds to the Late Pliensbachian Cold Event. This stratigraphic interval is also marked by low proportions of primary minerals (illite and chlorite) and the absence of kaolinite in several samples. It is interesting to compare clay mineralogy with palynological data, particularly with *Classopollis* proportions, the abundance of which is generally associated with warm and/or arid climates (Heimhofer *et al*., 2004; Van de Schootbrugge *et al*., 2005). *Classopollis* proportions (data from Van de Schootbrugge et al., 2005) are greater during smectite-rich or transitional intervals, while lower proportions of *Classopollis* are recorded during kaolinite-rich intervals. The number of samples studied having been analyzed palynologically is too small to establish a robust relationship between clay assemblages and

Classopollis proportions, but this first comparison would suggest that *Classopollis* abundance indicates more arid or semi-arid climate. Similar climatic conditions seem to have prevailed at the very beginning of the Pliensbachian (lowermost *jamesoni* Zone).

Finally, Pliensbachian climates appear to be characterized by alternating warm and humid periods (*davoei* Zone notably) and cooler and drier but seasonal periods (*subnodosus/gibbosus* subzones of the *margaritatus* Zone). This situation raises the question of the significance of the amplitude of $\delta^{18}O$ variations measured by various authors. In fact, the increase in temperatures causes an acceleration of the hydrological cycle, a greater hydrolysis and increased inputs of kaolinite. In this context, it may be wondered whether freshwater inputs into the marine environment have or have not led to a change in the $\delta^{18}O$ of sea water. If this is the case, the fluctuations of $\delta^{18}O$ in marine carbonates likely reflect both temperature and hydrological changes. For example, the decrease in $\delta^{18}O$ values in the *davoei* Zone considered particularly warm is possibly due in part to a decrease in $\delta^{18}O$ in sea water.

The spinatum *Zone*

The *spinatum* Zone interval shows a clay fraction with a specific mineralogical composition. This is characterized by the abundance of illite and R1 type illite-smectite (I-S) mixed-layers, and while the proportions of smectite are low, those of kaolinite are not very high. Compared to the underlying sediments, the *spinatum* Zone is characterized by the abundance of illite (secondarily chlorite), and R1 I-S. For the first time, the proportions of kaolinite increase parallel with those of illite. The relative abundance of primary minerals and R1I-S in comparison to smectite and kaolinite, suggests a deep physical erosion allowing only a moderate chemical weathering of illite and the formation of R1I-S. The co-variation of these minerals with kaolinite suggests that the latter could be mainly reworked from the previously deposited sediments, instead of from soils, along with illite and chlorite. Such an increase of

physical erosion is consistent with the substantial cooling, a slightly lower pCO_2 (Steinthorsdottir & Vajda, 2015) and a significant lowering of the sea-level. Interestingly, abundant illite and R1I-S occurs in the same aged rocks in the Paris Basin (Bougeault *et al*., 2017) and the Aquitaine Basin (south-western France, Brunel *et al*., 1999). As suggested by many authors, lowering of the sea-level could be a consequence of ice formation at high latitudes by the end of the Pliensbachian (Suan *et al*., 2010; Korte & Hesselbo, 2011; Silva & Duarte, 2015; Gómez *et al*., 2016a and b; Ruebsam *et al*., 2019). It is possible that lowering of sea-level led to the emergence of part of the continental shelf and that the kaolinite, and the small proportions of berthierine that is common in the *spinatum* Zone, were partially reworked from older Jurassic sediments (including incipient ironstones). The common occurrence of clinoptilolite could be a consequence of low sedimentation rate and/or enhanced productivity of siliceous organisms during colder climate conditions.

Differential settling processes

Kaolinite and, to a lesser extent, illite and chlorite, preferentially settle near shorelines, whereas smectite, given its smaller size and better buoyancy, is further exported to offshore environments (Gibbs, 1977; Chamley, 1989; Deconinck & Vanderaveroet, 1996; Hatem *et al*., 2017). Given the opposite evolution of the proportions of smectite and kaolinite, it is necessary to address the question of the possible role of differential settling processes of clay minerals in the marine environment. Clay mineral fractionation from land to offshore environments is enhanced especially when shallow rimmed carbonate platforms expand and retain kaolinite and/or chlorite in shallow environments (Deconinck *et al*., 1985; Godet *et al*., 2008). Sea-level changes may have played a significant role in Pliensbachian clay mineral sedimentation. Periods of high sea-level would have favoured a smectite-rich sedimentation following the increasing distance of the shoreline, in contrast to low-level periods being more

favourable to the sedimentation of kaolinite by decreasing the distance from the shoreline. However, comparing the evolution of clay assemblages with Early Jurassic sea-level curves inferred from detailed sequential analyses of British sections (Hesselbo & Jenkyns 1998; Van Buchem & Knox, 1998; Hesselbo, 2008), shows that fluctuations in the proportions of clay minerals are disconnected from sea-level changes except possibly during the *davoei* Zone where a lowering of sea-level may be responsible, at least in part, for the increase of kaolinite (Fig. 5).

CONCLUSIONS

The analysis of Pliensbachian clay mineral assemblages from the Llanbedr (Mochras Farm) borehole reveals that the clay minerals did not undergo significant transformations during their burial. This study did not reveal authigenic clay mineral phases, but zeolite from the clinoptilolite-heulandite group formed during periods of lower sedimentation rate, particularly in the latest Pliensbachian (*spinatum Zone*). The clay assemblages are mainly detrital, which allows their interpretation in terms of environmental changes. An antagonistic evolution of the proportions of smectite and kaolinite is interpreted mainly as the alternation of kaolinite-rich wet periods characterized by an acceleration of the hydrological cycle, and semi-arid periods rich in smectite during which the runoff and terrigenous inputs were smaller and carbonate sedimentation was better expressed. To this climatic control of the clay mineral sedimentation is presumably added a sea-level, possibly eustatic, control which is sometimes difficult to distinguish. An inferred sea level fall during the *davoei* Zone seems to be responsible in part for the increase in the proportions of kaolinite. However, the first-order variations in clay assemblages seem disconnected from changes in sea level in the *margaritatus* Zone where the more arid climatic conditions prevail. Finally, the clay mineral

assemblages of the *spinatum* Zone reflect an intensification of physical erosion, perfectly compatible with a significant lowering of the sea-level of possible glacio-eustatic origin.

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FIGURE CAPTIONS

Fig. 1. Location of the Llanbedr (Mochras Farm) borehole and simplified lithostratigraphy and biostratigraphy (ammonites) of the Pliensbachian succession. Abbreviations: To. – Toarcian; *br.- Brevispina; ja.- Jamesoni; ma. – Masseanum; lu. – Luridum; ml. - Maculatum; ca.- Capricornus; fi. – Figulinum; te. - Tenuicostatum.*

Fig. 2. Location of the Llanbedr (Mochras Farm) borehole on an Early Jurassic palaeogeography (modified from Blakey's palaeomap: https://deeptimemaps.com and Thierry *et al*., 2000). Abbreviations: SM - Scottish massif; IrM - Irish massif; CM - Cornubian massif; WM - Welsh Massif; LBM - London-Brabant Massif; RM - Rhenish Massif; BM - Bohemian Massif; MC - Massif Central; AM - Armorican Massif; IbM - Iberian Massif.

Fig. 3. Typical XRD diagrams of the clay fraction of the Pliensbachian sediments from Mochras. d values are given in Å. Abbreviations: Chl. - chlorite; Ill. - illite; I-S R0. - R0 type illite/smectite mixed-layers; K. - kaolinite; Be. - berthierine; Qz. - quartz; clino. - clinoptilolite-heulandite; F. - feldspar.

Fig. 4. Clay mineralogy of the Pliensbachian sediments of Mochras: I-S R0 corresponds to R0 type illite/smectite mixed-layers expanding to 17Å after glycolation and containing more than 50% of smectite layers. They are assimilated to smectite. I-S R1 corresponds to R1 type illite/smectite mixed-layers containing between 50% and 10% of smectite layers.

Fig. 5. Fluctuations of kaolinite/illite (K/I) and smectite/kaolinite (Sm/K) ratios and $CaCO_3$ content in the Pliensbachian of Mochras (this study) compared with *Classopollis* content (Van de Schootbrugge *et al.,* 2005) and inferred regional relative sea-level changes (Hesselbo, 2008) of Mochras. Hypothesized climatic intervals are also shown.

Fig. 6. Transmission electron microscopy images of some representative clay fractions. (A) Sample 4072.1 (1241.2 m depth; *jamesoni* Zone). The clay fraction is composed of dominant smectite (I-S R0) showing a fleecy shape characteristic of detrital particles with illite (ill.) and minor proportions of kaolinite and chlorite. (B) and (C) Sample 3438.6 (1048 m depth; *ibex* Zone), the clay fraction is dominantly composed of illite (ill.) with sharp outlines, kaolinite (K) with a sub-hexagonal shape, chlorite and small amounts of smectite (I-S R0). (D) Sample 3351.6 (1021.5 m depth; *davoei* Zone), mixture of illite, chlorite, kaolinite (K) and smectite (I-S R0) without any structure that would indicate authigenesis. Most particles shows irregular shape suggesting a detrital origin. (E) Sample 3092.1 (942.5 m depth; *margaritatus* Zone). The clay fraction is characterized by abundant smectite (I-S R0) showing a fleecy shape without any crystalline overgrowth. (F) Sample 3079.1. (938.5 m depth; *margaritatus* Zone) the clay fraction contains abundant smectite (I-S R0) showing a fleecy shape suggesting a detrital origin.